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(54) PRODUCTION OF OPTICAL MEMBER FOR EXCIMER LASER

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a quartz glass optical member having excellent stability for irradiation of UV laser, especially excimer laser such as KrF and ArF.
SOLUTION: The quartz glass is produced in the following processes. The starting source material obtd. from halogenated silicons, alkoxysilanes, alkylakoxysilanes or the like is subjected to oxidation heat treatment in the temp. range between ≥600° C and ≤1500° C to decrease the hydrogen concn. to ≤5 × 1016 molecules/cm3 as well as to decrease reducible defects. Then the quartz glass is kept at the temp. range between ≥200° C and ≤600° C in a hydrogen-contg. atmosphere to control the hydrogen concn. to ≥1 × 1017 molecules/cm3. Further, the quartz glass is treated to produce uniform distribution of the hydrogen concn. at the temp. range between ≥300° C and ≤800° C in an atmosphere of air, inert gas, hydrogen, mixture gas of hydrogen and inert gas, or mixture gas of air and inert gas. Thus, the quartz glass optical member having stable and excellent durability against laser can be obtd.

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* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of optical members made from quartz glass, such as a lens which constitutes the optical system of the laser-beam-machining equipment which makes said especially laser the light source, or lithography equipment, a mirror, and prism, about the manufacture approach of a quartz-glass optical member excellent in the stability over the exposure of excimer lasers, such as ultraviolet laser, especially KrF, ArF.
[0002]
[Description of the Prior Art] In recent years, since the short detailed drawing technique of line breadth is demanded more and it corresponds to this with high integration of LSI in the optical lithography technique which draws an integrated-circuit pattern on a wafer, short wavelength-ization of the exposure light source has been advanced. for this reason -- for example, the homogeneity and diactinism which the light source of the stepper for lithography excelled [excimer laser / (193nm) / the KrF excimer laser (248nm) from the G string (436nm) and i line (365nm) which have been used conventionally, and / ArF] in the lens which is going to be used and is used for a stepper very much have been required.
[0003] And in the wavelength field shorter than said i line (365nm), since light transmission nature sufficient in the multicomponent system optical glass used conventionally is not obtained, in order that quartz glass and it may also reduce ultraviolet absorption as much as possible, synthetic quartz glass with few impurity contents (synthetic silica glass) is used. In order to usually avoid mixing of the metal impurity leading to ultraviolet absorption, this synthetic quartz glass The volatile silicon compound of a high grade which was compounded chemically and purified by distillation, For example, halogenation silicons, such as a silicon tetrachloride (SiCl4), a tetra-ethoxy silane (Si4 (OC2H5)), The steam of alkyl alkoxysilane, such as alkoxysilane, such as a tetramethoxy silane (Si4 (OCH3)), and also methyl trimetoxysilane (SiCH3(OCH3) 3), is introduced into a direct acid hydrogen flame. It manufactures to transparent high grade quartz glass by carrying out melting deposition and growing up the glass particles which were made to carry out flame hydrolysis in an oxyhydrogen flame, and carried out decomposition generation here on the heat-resistant cylindrical core part material which rotates directly.
[0004] Moreover, after making it deposit as a particle as it is and forming a porosity silica base material on heat-resistant cylindrical core part material, without carrying out the direct melting deposition of the above-mentioned glass particles, there is also a method of carrying out the heating rarefaction of this porosity silica base material with an electric furnace, and acquiring a quartz-glass object. Thus, the manufactured synthetic quartz glass is a high grade very much, and since good light transmission nature is shown to an about 190nm short wavelength field, it is often used as excimer laser transparency ingredients, such as ultraviolet laser light, especially KrF, ArF.
[0005]
[Problem(s) to be Solved by the Invention] However, although the approach of improving the purity of synthetic quartz glass and raising the permeability of ultraviolet laser is effective to some extent, it may lack in dependability about the long-term exposure of ultraviolet laser, such as KrF and ArF. Since the energy per time amount is a very high light compared with the ultraviolet rays emitted from the usual mercury lamp etc. since excimer laser light is the pulsed light which has the pulse width which is extent for 20ns (nanosecond), this is because the load which joins glass becomes very large. in order to cancel this fault -- these people -- synthetic quartz glass -- the technique (Japan Japanese Patent Application No. 1-145226, USP5,086,352) which raises ultraviolet laser resistance is indicated especially by doping hydrogen gas inside of the body. This is a very effective means, in the case of the synthetic quartz glass which made hydrogen contain three or more 1x1017 molecule / cm, has arrived at the field satisfying as a material of the optical

member for KrF lithography, and, also industrially, is actually carried out as an effective means.
[0006] And the technique of heating synthetic quartz glass in ordinary pressure thru/or a pressurization hydrogen gas ambient atmosphere as a means to dope said hydrogen gas is indicated by said application. Moreover, such a hydrogen gas doping technique is indicated by Japan JP,1-201664,A, and the technique which made said gas doping possible is indicated by heat-treating at 800-1000 degrees C under an ordinary pressure hydrogen gas ambient atmosphere especially in this official report. Now, although said application was the technique to which its attention was paid about hydrogen gas concentration or OH radical concentration, when this invention person investigated in the detail more about the behavior of the paramagnetism defect generated by laser radiation and predetermined concentration content of the hydrogen was carried out, generation of a paramagnetism defect is not controlled with all quartz glass, and it became clear that it had variation with a material. And since it becomes the variation in the life of an optical member as it is, the difference of this laser resistance produces disadvantageous profit industrially.
[0007] Furthermore, by the KrF (248nm) laser from which it is comparatively separated in wavelength, since the paramagnetism defect produced by laser radiation has [215nm] the peak of absorption, even when it does not become a problem so much, in the case of ArF (193nm) laser near in wavelength, it poses a big problem. Now, since excimer laser light like ArF and KrF has the very high energy as a light, a chemical bond can be cut directly and neither punching processing using excimer laser light nor stripping processing of a wire is accompanied by early and heat compared with the conventional YAG laser and carbon dioxide laser for this reason, it is the field from which has an advantage, like it can do correctly and application in the industrial world will be expected from now on.
[0008] However, since the ingredient which constitutes the optical system used for these applications had the very high luminous energy consistency used when a penetrable good ingredient is limited to synthetic quartz glass, since such light is ultraviolet rays, even if it was synthetic quartz glass, it produced the optical damage immediately and had the problem of endurance. Since the excimer laser luminous energy demanded especially in laser ablation processing requires the energy which is sufficient for the polyimide metallurgy group by which ablation is carried out decomposing by light, and evaporating, it is extraordinarily powerful. Sufficient effectiveness will not be acquired even if using an optical member which is used for such a technical field for example, with excimer laser lithography is equipped with laser resistance with it sufficient as a lens material for lithography.
[0009]
[Means for Solving the Problem] This invention aims at offering the manufacture approach of the excimer laser-proof which controlled the variation in said paramagnetism defective generation at the time of laser radiation, was stabilized more in view of the fault of this conventional technique, and was excellent in laser resistance especially ArF, and the optical member for KrF excimer laser. The place made into other purposes of this invention is to offer the manufacture approach of an optical member suitable as an optical member used for an excimer laser ablation processing machine that especially long-term use can also attain sufficient optical stability. The place made into other purposes of this invention is to offer an optical member suitable as an optical member used for lithography equipment.
[0010] In the quartz glass for ultraviolet laser-proof which used as the start base material wholeheartedly the transparent glass which comes to carry out the melting deposition of the glass particles as a result of research in order that this invention persons might solve this problem The improvement effectiveness of the laser resistance by hydrogen content is not simply decided only by hydrogen concentration. It traces that it is dependent on the condition of the quartz glass at the time of said hydrogen being introduced (dope), and the temperature into which hydrogen is introduced. In addition to the setup of the optimal hydrogen concentration, it found out that the purpose of this invention was attained for the first time specifying a setup of the condition of the quartz glass before hydrogen installation, and the introductory temperature of hydrogen, and by achieving equalization of concentration distribution of the hydrogen introduced further.
[0011] That is, in order that the synthetic quartz obtained by carrying out direct melting deposition on a base may compound a silica particle by the acid hydrogen flame, the hydrogen of remarkable concentration is already dissolved in the manufactured phase in many cases, and the concentration may also contain three or more cm [1x1018 molecule / cm] hydrogen, when many. And in such quartz glass, since the temperature into which hydrogen is introduced was very high, it became clear that the defect of the reducibility by hydrogen arose at the time of synthetic quartz manufacture. For this reason, in such quartz glass, even if, although hydrogen concentration was high, when an excimer laser is irradiated, the defect which has an absorption peak in 215nm called E* center will generate promptly, and the permeability of laser will fall rapidly.
[0012] Then, this invention carries out oxidation heat treatment of the start base material obtained from said halogenation silicons, alkoxysilane, and alkyl alkoxysilane in a temperature field (600 degrees C or more and 1500 degrees C or less), and is characterized [1st] by reducing the reducibility defect described above while making three or

less 5x1016 molecule / cm reduce hydrogen concentration. Although the oxygen deficiency mold defect was generally typical as a reducibility defect, since this defect had absorption to the 245nm wavelength field, when the internal transmittance in this wavelength was 99% or more per 1cm of samples, it turned out substantially that it can be considered that the reducibility defect has been eliminated.

[0013] The internal transmittance said here is the value which expressed the appearance permeability per cm in sample thickness with theoretical permeability. Moreover, in the suitable temperature conditions for said reducibility defective removal, since distorted removal of quartz glass is also possible, if these two processes are performed to coincidence at coincidence, it is efficient. In the desirable example of this invention as the 1st process then, said reducibility defect, especially oxygen deficiency removal By annealing 800-1500 degrees C in the ambient atmosphere which has oxygen, after holding preferably in a temperature field 1000 degrees C - 1300 degrees C or less, with distorted removal It is the 1st description to try for the hydrogen concentration which the internal transmittance to ultraviolet rays with a wavelength of 245nm is 99.8% or more, and is contained to reduce three or less 5x1016 molecule / cm.

[0014] Next, although it was the translation which makes hydrogen concentration contain three or more 1x1017 molecule / cm at the 2nd process, in order to bring a dope rate forward in this case, when hydrogen installation was performed by the pyrosphere, it became clear by experiment that the defect of new reducibility arose. Then, this invention is characterized [2nd] by holding quartz glass under a hydrogen content ambient atmosphere to 200-degree-C or more temperature field 600 degrees C or less, and making hydrogen concentration contain three or more 1x1017 molecule / cm. That is, if hydrogen doping is performed at the elevated temperature exceeding 600 degrees C, the reducibility defect by the reaction of quartz glass and hydrogen will generate, and since the diffusion rate of hydrogen gas to quartz glass is slow, with hydrogen doping at the temperature of less than 200 degrees C, doping in the economical range will become difficult industrially.

[0015] In addition, since the stability over laser increases so that hydrogen concentration is high when hydrogen is made to dope at the temperature of 600 degrees C or less after performing oxidation treatment as shown by this invention, the hydrogen pressure force in the case of a hydrogen dope is so desirable that it is high. Ten or more atms of things to carry out by the pressure preferably exceeding 50atm(s) are required for hydrogen doping in a temperature field 600 degrees C or less in high-pressure furnaces, such as an autoclave, in fact. Now, after heat-treating the ingot in which these people have OH radical concentration in Japan JP,3-23236,A previously in an oxygen gas ambient atmosphere as a technique similar to this invention, the technique heat-treated at about 600 thru/or 700 degrees C by the hydrogen gas ambient atmosphere is proposed.

[0016] However, it is characterized by performing hydrogen doping so that this invention may eliminate the defect on the other hand paying attention to the reducibility defect produced by the reaction of quartz glass and hydrogen for the purpose of said technique only removing an oxygen deficiency by oxidation heat treatment and these defects may not generate again. Furthermore, although these people are indicating the technique of heating said silica glass at 200 thru/or 1200 degrees C in ordinary pressure thru/or a pressurization hydrogen gas ambient atmosphere as a means to dope hydrogen gas, in Japan JP,3-88742,A After this invention removes a reducibility defect in advance of hydrogen doping to this technique having only regulated the temperature requirement which hydrogen can dope, it is characterized by performing hydrogen doping in the temperature field which a reducibility defect does not generate again.

[0017] That is, this invention be characterize by the point which carry out hydrogen installation so that a reducibility defect may not arise at the reducibility defect include in the synthetic quartz glass obtain by carrying out the direct melting deposition of the silica particle on a base, the process which remove hydrogen first, and the 2nd process, and the combination of these two processes be needed first. However, the concentration of the circumference part is higher than the concentration of a core as a result by which hydrogen concentration distribution of the quartz glass containing the high-concentration hydrogen obtained by doing in this way is based on the principle of a diffusion phenomenon. this -- also taking -- it does not correct, but it has the-like-proportionally effect on distribution of a refractive index, and the homogeneity originally needed is checked. Then, according to the 3rd process, this invention is characterized by achieving equalization of introductory hydrogen concentration.

[0018] That is, predetermined time maintenance is carried out as the 3rd process which is the last step of this invention in 300-degree-C or more temperature requirement 800 degrees C or less in the mixed gas of air, inert gas, hydrogen or hydrogen, and inert gas, or air and the mixed-gas ambient atmosphere of inert gas, and it is characterized [3rd] by performing hydrogen concentration equalization processing. This invention will not be able to attain the purpose of this invention without performing said 1st, 2nd, and 3rd processes one by one. Thus, offer of the synthetic quartz glass optical member for ultraviolet laser which sets hydrogen concentration to three or more 1x1019 molecule / cm preferably three or more 1x1017 molecule / cm, and has uniform refractive-index distribution of this invention was

attained, eliminating a reducibility defect.
[0019] And when using said optical member for an excimer laser ablation processing machine, in order that especially this invention person may realize high endurance especially over the excimer laser of high power As a result of adding research wholeheartedly, volatile silicon compounds, such as a tetramethoxy silane, with the combustible-gas flame containing hydrogen, such as oxygen, a hydrogen flame or oxygen, and methane The OH radical concentration obtained by depositing on the base turning around the silica particle obtained by carrying out flame hydrolysis, and fusing uses synthetic quartz glass 500 ppm or more as a start base material. In the ambient atmosphere which contains oxygen for this after adding a twist and performing homogenization in at least 1 direction, performing zone melting for this start base material by the zone-of-melting region method according to a case (it is good also in the usual atmospheric-air ambient atmosphere.) 800 degrees C - 1500 degrees C are heated preferably in a 800 degrees C - 1300 degrees C temperature requirement. After setting the hydrogen concentration to contain as three or less 1x1016 molecule / cm, it is the high pressure of 50 or more atms preferably 10 atms about hydrogen in an autoclave. And 200 degrees C or more 600 degrees C or less of hydrogen are preferably doped at the temperature of 300 to 450 degrees C. Content hydrogen concentration is set to three or more 1x1019 molecule / cm. Further Air, inert gas, By carrying out predetermined time maintenance in 300-degree-C or more temperature requirement 800 degrees C or less in the mixed gas of hydrogen or hydrogen, and inert gas, or air and the mixed-gas ambient atmosphere of inert gas, and carrying out hydrogen concentration equalization processing Even when it used for an excimer laser ablation processing machine, it found out that the optical member which fully has endurance could be obtained.
[0020] In case according to another technique homogenization of starting material does not take a special processing step but carries out the melting deposition of the direct hydrolyzate in the inside of an oxyhydrogen flame on a rotation base, it may use the quartz glass grown up and obtained, maintaining uniform refractive-index distribution by controlling temperature conditions and other growth conditions. At this time, it is preferably good for quartz glass to use the silanes, methyl trimetoxysilane SiCH3(OCH3) 3 [for example,], which do not contain chlorine, the tetra-ethoxy silane (OC2H5) Si 4 or hexa methyl disiloxane Si 2O(CH3) 6, etc. as an volatile silicon compound which is the purpose which eliminates the effect of the chlorine contained as an impurity as much as possible, and is the raw material of synthetic quartz glass.
[0021]
[Embodiment of the Invention] Hereafter, based on a drawing, the example of this invention is explained in detail in instantiation. However, the quality of the material of the component indicated by this example, a configuration, its presentation, etc. are not the meaning that limits the range of this invention only to it but only the mere examples of explanation, as long as there is no specific publication especially.
[0022] The manufacture approach of the synthetic quartz glass first used for this invention is explained. The exertion nature silicon compound of the high grade which was chemically compounded by the volatile silicon compound used for composition, and was therefore purified by distillation, For example, halogenation silicons, such as a silicon tetrachloride (SiCl4), a tetra-ethoxy silane (Si4 (OC2H5)), Siloxanes, such as alkyl alkoxysilane, such as alkoxysilane, such as a tetramethoxy silane (Si4 (OCH3)), and methyl trimetoxysilane (SiCH3(OCH3) 3), and hexa methyl disiloxane (Si 2O(CH3) 6), are used.
[0023] Under the present circumstances, chlorine remains and is not desirable on the synthetic quartz glass generated when the volatile compound of Cl content, such as a silicon tetrachloride (SiCl4), was used. And it deposited on the target turning around the silica particle obtained by carrying out flame hydrolysis of the methyl trimetoxysilane (SiCH3 (OCH3) 3) of a high grade, for example by the acid hydrogen flame, fused, and the synthetic quartz glass ingot with an outer diameter [of 100mm] and a die length of 800mm was generated. The absorption intensity of 3800cm-1 according [the OH radical concentration contained in an ingot at this time] to infrared spectrophotometry showed that it was 600 ppm. moreover, the hydrogen concentration contained when the hydrogen content child concentration contained in this ingot is measured with Raman-scattering spectrophotometric analysis -- 2x1018 molecule / cm3 it was . a use device -- the product made from the Jasco industry -- the output used 700mW and Hamamatsu Photonics R943 -02 photomultiplier by Ar laser with a NR-1000 and an excitation wavelength of 488nm, and it measured in HOTON counting.
[0024] In addition, the content hydrogen concentration in the quartz glass in this invention is Zhurmal Prikladonoi Spektroskopii Vol.46 No.6 pp987 to 991 june 1987. It was based on the approach shown. That is, it asks for the hydrogen content child concentration in quartz glass by the reinforcement of the Raman band of wave number 800cm-1 about SiO2, and the intensity ratio of 4135cm-1 about the hydrogen content child who contains in quartz glass, and the hydrogen content child concentration C is computed by the following formulas (1).
C=K (I4135/I800) -- (1)

It is among a formula (1) and is K:constant (1.22x1021).
I4135: It is the integrated intensity of the Raman band of 4135cm-1.
It is the integrated intensity of the Raman band of I800:800cm-1.
The hydrogen content child concentration computed by this formula is a hydrogen content child's number contained in the quartz glass per volume of 3 1cm.
[0025] As shown in drawing 5 , the bearing bar 32 of the quartz glass of the diameter of said was welded to the both ends of this synthetic quartz glass ingot 30, and both-ends grasping was carried out by the chucks 31 and 31 of a stria stripper shown in drawing 5 . Synchronizing rotation of the chucks 31 and 31 of these right and left, and carrying out predetermined include-angle round trip rotation of the synthetic quartz glass ingot 30, that edge was strong-heated with oxygen / hydrogen burner 34, and the zone-of-melting region was formed. After zone-of-melting region 30a was formed, it kneaded by scouring to the quartz glass in zone-of-melting region 30a in a hoop direction, and giving the lump force by rotating rotation of the chucks 31 and 31 of said right and left in the direction in which each faces. 35 is a motor which carries out both-way rotation of the chuck 31.
[0026] Next, the synthetic quartz glass ingot 30 whole was homogenized by moving oxygen / hydrogen burner 34 to the other end side of the synthetic quartz glass ingot 30 slowly. The synthetic quartz glass ingot 30 was separated from the bearing bar 32 after homogenization, and although the stria at the time of seeing to the revolving shaft and perpendicular of an ingot was observed when the sample was started and the stria was observed, the stria was not observed in the direction of a cross section of an ingot. Two or more synthetic quartz vitreous humours which finished this homogenization were started to discoid with an outer diameter [of 100mm], and a thickness of 15mm, and were divided into the sample A group and B group, respectively. After cooling slowly to 200 degrees C after 48-hour heating at 1000 degrees C within the electric furnace of an atmospheric-air ambient atmosphere about a sample A group, radiationnal-cooling cooling was carried out and reducibility defective removal processing was performed. The sample B group did not perform this reducibility defective removal processing, but used it for the following process.
[0027] After cooling, when the hydrogen concentration of each sample was measured with Raman-scattering spectrophotometric analysis, hydrogen concentration was three or less the 1x1016 molecule / cm which is the limit of detection of this measuring method, and the internal transmittance in 245nm was 99.9%/cm. Subsequently, it installs in the autoclave furnace which shows a sample A-9 to drawing 4 , and is abbreviation 100atm. High-pressure hydrogen gas enclosed, and when the temperature up was carried out to 300 degrees C, the pressure up of the internal atmospheric pressure was carried out to abbreviation 200atm. It held in the condition of this as for 720 hours. the place which measured the hydrogen concentration of the sample A-9 after processing with Raman-scattering spectrophotometric analysis -- 8.9x1019 molecule / cm3 it is -- things were understood.
[0028] An autoclave furnace consists of the head section 42 made from stainless steel which closes the furnace body 40 made from stainless steel, the heater 41 which surrounds the perimeter, and top-face opening of said furnace body 40 as shown in drawing 4 , and the hydrogen circuit 43 and the pressure gage 44 are attached in said head section 42. 45 is a sample for carrying out hydrogen processing. The high-pressure hydrogen gas of abbreviation 50atm enclosed the sample A-2, and when the temperature up was carried out to 300 degrees C, the pressure up of the internal atmospheric pressure was carried out to abbreviation 100atm. It held in the condition of this as for 720 hours. the place which measured the hydrogen concentration of the sample A-2 after processing with Raman-scattering spectrophotometric analysis -- 5.5x1019 molecule / cm3 it is -- things were understood.
[0029] the place which enclosed hydrogen with the high-pressure hydrogen gas of abbreviation 30atm, and carried out the temperature up of the furnace temperature to 400 degrees C about the sample A-3 -- an internal atmospheric pressure -- abbreviation 100atm up to -- the pressure up was carried out. It cooled slowly after 120-hour maintenance in the condition of this as. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 5.1x1019 molecule / cm3. the place which enclosed hydrogen with the high-pressure hydrogen gas of abbreviation 30atm, and carried out the temperature up of the furnace temperature to 400 degrees C about the sample A-4 -- an internal atmospheric pressure -- abbreviation 100atm up to -- the pressure up was carried out. In the condition of this as, it cooled slowly after 48-hour maintenance. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 5.0x1019 molecule / cm3.
[0030] the place which enclosed hydrogen with the high-pressure hydrogen gas of abbreviation 25atm, and carried out the temperature up of the furnace temperature to 800 degrees C about the sample A-5 -- an internal atmospheric pressure -- abbreviation 100atm up to -- the pressure up was carried out. It cooled slowly after 24-hour maintenance in the condition of this as. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 5.2x1019 molecule / cm3. About a sample A-6, it is

1atm about hydrogen. The temperature up of the furnace temperature was carried out to 300 degrees C with the sink in the condition, and it cooled slowly after 720-hour maintenance in the condition of this as. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 2.1x1017 molecule / cm3.

[0031] When the hydrogen gas of abbreviation 5atm enclosed hydrogen and the temperature up of the furnace temperature was carried out to 300 degrees C about the sample A-7, the pressure up of the internal atmospheric pressure was carried out to abbreviation 10atm. It cooled slowly after 720-hour maintenance in the condition of this as. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 1.2x1018 molecule / cm3. When the high-pressure hydrogen gas of abbreviation 25atm enclosed hydrogen and the temperature up of the furnace temperature was carried out to 300 degrees C about the sample A-8, the pressure up of the internal atmospheric pressure was carried out to abbreviation 50atm. It cooled slowly after 720-hour maintenance in the condition of this as. When the hydrogen concentration of the sample after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 3.2x1019 molecule / cm3.

[0032] It was the example of a comparison which performs neither said reducibility defective removal processing nor hydrogen dope processing about a sample B-1, and since it strong-heated with oxygen/hydrogen burner in this case and the zone-of-melting region was formed, hydrogen concentration was 1x1018 molecule / cm3. Next, it is abbreviation 50atm like [sample / B-2 / said] a sample A-2. High-pressure hydrogen gas enclosed, and when the temperature up was carried out to 300 degrees C, the pressure up of the internal atmospheric pressure was carried out to abbreviation 100atm. It held in the condition of this as for 720 hours. When the hydrogen concentration of the sample B-2 after processing was measured with Raman-scattering spectrophotometric analysis, it turned out that they are 5.4x1019 molecule / cm3.

[0033] Next, in order to evaluate a laser-proof property about said each sample, ArF excimer laser light was irradiated at said each sample, and change of the absorbance in 215nm which is absorption of a paramagnetism defect (E* center) was measured. Absorbance of 215nm - It calculated using log (internal transmittance per cm). Next, said transmissometry approach is explained to a detail. Drawing 6 is the schematic diagram of transmissometry equipment, and 1 is excimer laser, and using LPX2000 by Lambda Physik A.G., it is constituted so that laser radiation may be carried out to a right angle in energy density 200mJ/cm2p per pulse, and 100Hz in the laser radiation side of each sample 75.

[0034] Transmissometry equipment is constituted by the photomultiplier 78 for measuring the 2nd monochromator 76 and quantity of light to penetrate on both sides of the 1st photomultiplier 74 for measuring the quantity of light of incident light through D2 lamp 73, the 1st monochromator 71 which carries out the spectrum of the light to 215nm, and a beam splitter 72 as the light source of ultraviolet rays, and a sample 75. the light irradiated from D2 lamp 73 -- a beam splitter 72 -- minding -- a part -- while carrying out incidence to a photomultiplier 74, the spectrum of other light should be carried out to 215nm by the monochromator 71, and they should pass the 75 monochromator sample 76 -- light is received by the photomultiplier 78 and permeability can be measured by the light-receiving ratio of photomultipliers 78 and 74. Since measurement of the light income of photomultipliers 78 and 74 synchronizes with the oscillation pulse of an excimer laser, it can measure permeability to coincidence here, performing laser radiation.

[0035] And using said equipment, it measures for every exposure pulse from the side face of the direction of laser radiation about each sample, and the internal transmittance change is shown in drawing 1 thru/or drawing 3 . In addition, on the same wavelength of 193nm as exposure laser, since equipment was damaged, the measured permeability measured the permeability of 215nm which is the absorption wavelength of E* center. It is **, and since proportionality is with an absorbance [of 215nm], and an absorbance of 193nm in between in fact, the internal translucent rate of the quartz glass under laser radiation can actually be obtained with said measuring method.

[0036] Drawing 2 shows internal transmittance change of the sample A-2 thru/or sample A-5 based on the difference in the processing temperature in a hydrogen processing furnace. As being understood from this Fig. etc., About the sample A-2 whose dope temperature is 300 thru/or 400 degrees C, and A-3, it sets in an initial property (exposure pulse number: 2x104 to 6x104). As internal transmittance showed a **** middle property (exposure pulse number: 1x105) further to drawing 1 or more by 0.98 (O), also in a property (exposure pulse number: 1x107), internal transmittance is 0.96-0.98 (O) over a long period of time, and desirable laser-proof evaluation was able to be obtained.

[0037] in addition, internal transmittance -- 0.98 or more -- (O) internal transmittance -- (**) internal transmittance makes [0.96-0.98 / (O) and internal transmittance] 0.94 or less (x) for 0.94-0.96. Moreover, about that (sample A-5) whose dope temperature is 800 degrees C, internal transmittance fell to 0.94-0.96 (**) in the initial property, and as shown in drawing 1 after that, internal transmittance remained in 0.94-0.96 (**) also in the property over a long period

of time. Moreover, about what performed only reducibility defective removal processing, without performing a hydrogen dope (sample A-1), although the range of internal transmittance was 0.94-0.96 (**) in the initial property, internal transmittance fell gradually after that, as shown in drawing 1 , internal transmittance was falling below to 0.94 (x) in the property over a long period of time, and neither was able to obtain laser-proof evaluation.

[0038] Moreover, as internal transmittance fell to 0.96-0.98 (O) in an initial property about a 600-degree C thing (sample A-4) and it was shown in drawing 1 , internal transmittance also remained in the same level as 0.96-0.98 (O) in the property over a long period of time. Although internal transmittance is falling sharply about the sample B-1 and the sample B-2 in an initial property (exposure pulse number: 2x104 to 6x104) since all omit reducibility defective removal processing Having recovered quickly after that was understood and it was checked that said sample B-2 (5.4x1019 molecule / cm3) of extent of the recovery is better than a sample B-1 (1.0x1018 molecule / cm3) corresponding to hydrogen concentration.

[0039] and about said sample B-2, it was checked by drawing 1 that the internal transmittance in 215nm after 107 pulse irradiation is carrying out until [comparable] recovery with the sample A-8. the variation [ArF laser (200mJ/cm2p --) of the hydrogen concentration based on change of the hydrogen processing pressure force in drawing 3 , and internal transmittance 100Hz shows variation (permeability [before laser radiation], and difference deltaT% of permeability after long-term exposure)] of the internal transmittance in 215nm before and behind 107 pulse irradiation. Although internal transmittance with a dope pressure desirable in 100 or more (a sample A-2, sample A-9) atms could be obtained and the dope pressure was the fall of the range where the sample A-8 of 50atm(s) does not interfere practically, either as understood from this Fig. etc. a dope pressure -- the thing (a sample A-6, A-7) of 10 or less atms -- the decline in internal transmittance -- large -- especially -- a sample A-6 -- internal transmittance -- below 0.94 (x) -- moreover, internal transmittance was falling or less to 0.94 (x) also about the sample A-7.

[0040] Now, since the laser output is needed before and after 100 - 700 mJ/cm2p when using it for an excimer laser ablation processing machine After heating preferably in a 800 degrees C - 1300 degrees C temperature requirement and carrying out reducibility defective removal processing (the hydrogen concentration to contain is set as three or less 1x1016 molecule / cm) in the ambient atmosphere containing the above mentioned oxygen, hydrogen 50atm(s), By being the high pressure of 100 or more atms preferably, and doping preferably 600 degrees C or less of hydrogen at the temperature before and behind 300-450 degrees C of abbreviation, and setting content hydrogen concentration as three or more 1x1019 molecule / cm Although the optical member which fully has endurance can be obtained even when it uses for an excimer laser ablation processing machine About the optical member used for lithography equipment on the other hand, since the laser output is good before and behind 1 - 10 mJ/cm2p, the optical member which has the laser-proof [high power] nature described above not necessarily is not needed.

[0041] then, this invention about the sample A-4 made not desirable by said evaluation trial, a sample A-5, a sample A-6, a sample A-7, and a sample B-2 The variation of hydrogen concentration and internal transmittance based on the condition of the existence of the reducibility defective processing before change of the hydrogen processing pressure force / temperature, and hydrogen dope processing When change of internal transmittance [in / for the energy of a laser beam / 215nm after 107 pulse irradiation] is checked by [ArF laser (20mJ/cm2p, 100Hz) by 1/10 of laser outputs from last time, as shown in drawing 1 although internal transmittance (O->O) also with that (sample A-4) desirable whose dope temperature is 600 degrees C was able to be obtained -- a 800-degree C thing (sample A-5) -- from the time of an initial property -- small -- having recovered (**->O) -- desirable laser-proof evaluation was not able to be obtained.

[0042] Moreover, when dope temperature was 300 thru/or 600 degrees C, internal transmittance (O->O) with a dope pressure desirable in 10 or more (sample A-7) atms could be obtained, and it was the fall of the range which a dope pressure can use somehow although the sample A-6 of 1atm also fell from the initial property (O) to the property (**) over a long period of time. Moreover, even if it had three or more cm [5x1019 molecule / cm] hydrogen concentration about the sample B-2 which performed only hydrogen dope processing, without perform reducibility defective processing also about the condition of the existence of the reducibility defective processing before hydrogen dope processing, it was not able to fall sharply at the time of an initial property (x), and laser-proof evaluation desirable as highly precise lithography equipment was not able to be obtained.

[0043] It is an element important in respect of resolution that a refractive index is homogeneity (the same) also in which part of that optical path, and it means the good permeability in operating wavelength and its durability (the so-called resistance) are not only required for an optical member, but that these three elements had filled the demand as an optic for the first time together to the light to penetrate as described above. Since the need for the 1st process which this invention person asserts in the example of until said, and the 2nd process (permeability and durability) became clear, an example explains further the place for which the optical member which raised hydrogen concentration, without next making a reducibility defect generate again by the low-temperature high concentration hydrogen dope needs the

actuation which equalizes hydrogen concentration distribution according to the 3rd process.
[0044] That is, flame hydrolysis of the direct volatility silicon compound was carried out for the volatile silicon compound, heating molding was carried out at 1800 degrees C using the graphite mold in the furnace which homogenized and carried out the nitrogen purge of the synthetic quartz obtained by carrying out melting and deposition on the base which rotates the silica particle to generate as it is by the zone melting, and quartz-glass molding object plurality with an outer diameter [of 100mm] and a thickness of 50mm was obtained. the homogeneity of the refractive index which anneals this molding object after 10-hour heating at 1150 degrees C, and does not have a stria in the use direction -- the quantity of deltan5x10-6 -- the homogeneous quartz-glass member was obtained. Let this be a sample C group. The condition of being one of the sample C groups to which the homogeneous refractive index has appeared in drawing 10 is shown.
[0045] Subsequently, the sample C group was annealed with the cooling rate of 5 degrees C per time amount after 50-hour heating at 1150 degrees C among atmospheric air. The hydrogen concentration of a member was three or less 5x1016 molecule / cm. (The 1st process)
The sample C group which passed through the 1st process was heated at 100atm(s) and 500 degrees C all over the pressurization hydrogen furnace for 500 hours. Although center sections were 7x1018 molecule / cm3 when the hydrogen concentration of the obtained quartz-glass member was measured, in the 20mm part, 2.5x1019 molecule / cm3, and a 3.5 times as many concentration difference as this were accepted from the periphery. In connection with this, the periphery became very high [refractive-index distribution], and deltan was set to the level which cannot be practically used as that of 2x10-5, and an optic. The condition is shown in drawing 11 . (The 2nd process)
[0046] Heat treatment of 50 hours - 400 hours was performed for the sample C group which passed through the 1st process and the 2nd process at 500 degrees C among atmospheric air (the 3rd process). Corresponding to the processing time, it was referred to as a sample C-1, C-2, C-3, C-4, and C-5, respectively, and the result of the hydrogen concentration distribution was shown in drawing 8 . Since processing is insufficient, if the improvement of deltan is inadequate and it exceeds 300 hours, an improvement of refractive-index distribution will not be accepted any more, but it turns out that hydrogen concentration is moreover falling in 50 hours equivalent to a sample C-1. Drawing 12 is the interference fringe pattern Fig. of the 3rd process, and shows the condition of uniform hydrogen concentration distribution being acquired and requiring it. Although similarly heat-treated at 600 degrees C among atmospheric air, when each processing time was carried out in 60 hours, 120 hours, 180 hours, and 240 hours, the improvement of deltan which should be satisfied similarly was obtained.
[0047] Now, when the suitable conditions of hydrogen concentration equalization processing were explored experimentally in this way, naturally, it was related to the temperature dependence of the diffusion rate in the inside of the quartz of hydrogen, and this invention person also found out that there was the suitable processing-time range of the 3rd process by the temperature gradient of the temperature in the 2nd process, and the 3rd process. When were quantitatively specified from diffusion theory, and the 3rd process was performed at temperature higher than the temperature of the 2nd process among 500-degree-C or more temperature requirement 800 degrees C or less and the processing temperature gradient of the 2nd process and the 3rd process was set to deltaT for the processing time, delta (0.6) T/more than 100x20%(0.6) deltaT of the processing time of the 2nd process / 100x40% or less of range was suitable. Drawing 7 shows an example of an ablation processing machine by the excimer laser to which the optical member of this invention is applied.
[0048] Drawing 7 is equipment which performs hole dawn for connection between wiring layers (VIA hole processing) to the interlayer insulation film of a multilayer-interconnection substrate, in 51 in drawing, a mirror and 53 are quartz-glass substrates, a focusing lens and 54 put [a collimate lens and 55] the copper (Cu) film 56 with a thickness of 2 micrometers by the spatter on this glass substrate 55, and a laser oscillation machine and 52 cover the polyimide film as resin film 57 with a thickness of 40 micrometers on it. Besides, a mask 58 is set and piled up and spacing of 0.4mm is fixed for it on X-Y stage 59. In addition, said mask 58 forms dielectric multilayers 58B which has a hole pattern with a diameter of 40 micrometers on synthetic quartz substrate 58A.
[0049] And what was manufactured in this equipment by the optical member which formed said mirror 52, the focusing lens 53, and the collimate lens 54 by the sample C-2 or sample C-4 of this example is attached. While oscillating excimer laser from said laser oscillation machine 51 on the oscillation wavelength of 248nm (KrF), output 300mJ/cm2p, and the frequency of 200Hz Said mirror 52 and lens systems 53 and 54 are minded. Turning of this laser, while performing focusing and collimation-ization and moving X-Y stage 59 according to the hole pattern of said mask 58 -- said glass substrate 55 -- a step-and-repeat method -- scan processing -- carrying out -- and said scan processing -- repeating -- many, although carried out about several glass substrates It has checked that an accurate through tube generated, without damage arising on said resin film 57 at the substrate copper film 56.

[Translation done.]

* NOTICES *

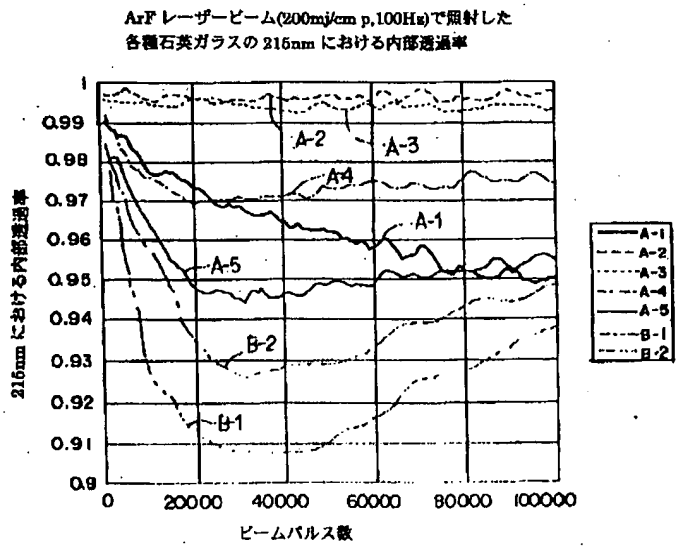
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

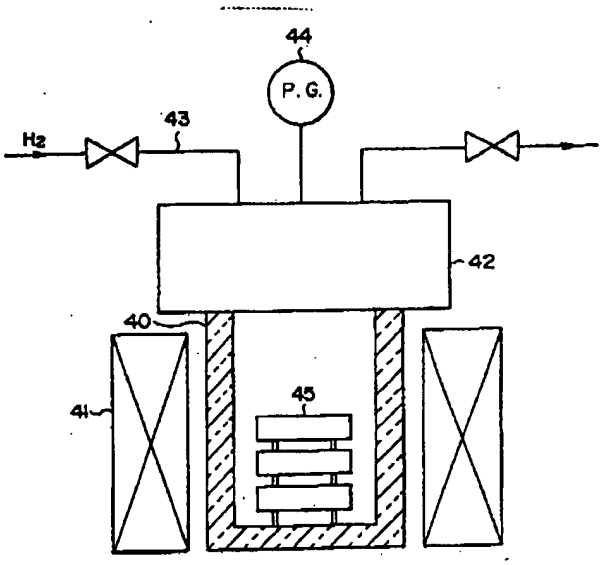
[Drawing 1]

SAMPLE No.	真空紫外線吸収工程	水素濃度 (MOLECULES/cm³)	ドープ温度 (℃)	ドープ圧力 (atm)	ドープ時間 (Hr.)	耐レーザー評価 初期→長期 (200 mJ/cm²p)	耐レーザー評価 初期→長期 (20 mJ/cm²p)
A-1	○	$<1\times10^{16}$	–	–	–	△→×	–
A-2	○	5.5×10^{16}	300	100	720	◎→○	–
A-3	○	5.1×10^{16}	400	100	120	◎→○	–
A-4	○	5.0×10^{16}	600	100	48	○→○	◎→◎
A-5	○	5.2×10^{16}	800	100	24	△→△	△→○
A-6	○	2.1×10^{17}	300	1	720	◎→×	◎→△
A-7	○	1.2×10^{16}	300	10	720	◎→×	◎→○
A-8	○	3.2×10^{16}	300	50	720	◎→△	◎→◎
A-9	○	8.9×10^{16}	300	200	720	◎→○	–
B-1	×	1.0×10^{16}	–	–	–	×→△	–
B-2	×	5.4×10^{16}	300	100	720	×→○	×→◎

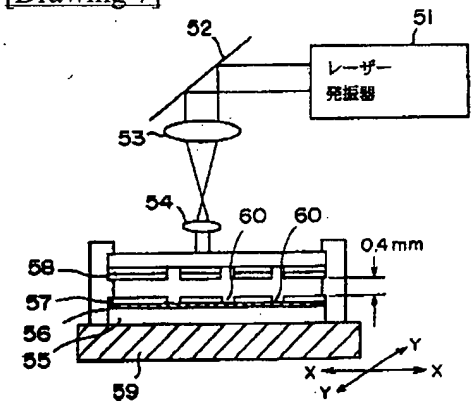
[Drawing 2]



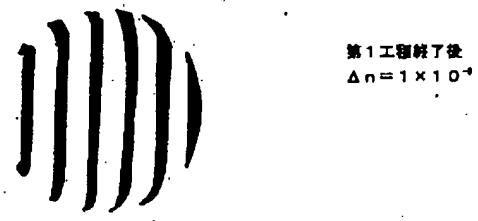
[Drawing 4]



[Drawing 7]



[Drawing 10]

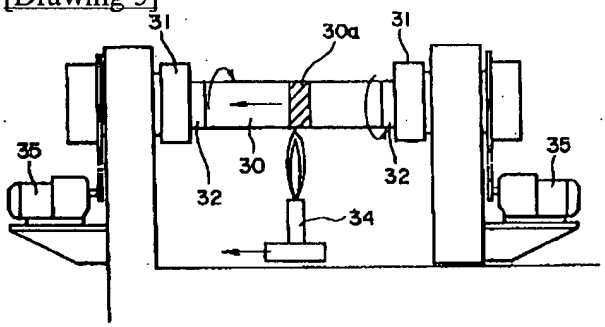


[Drawing 11]

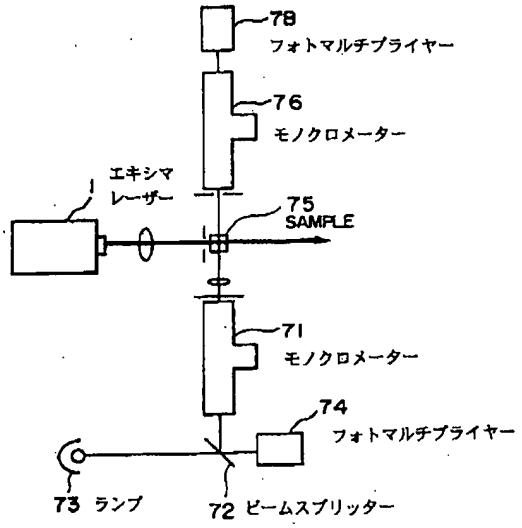
[Drawing 3]

SAMPLE No.	水素ドープ圧力 (気圧)	水素濃度 (MOLECULES/cm³)	還元性欠陥除去工程	ArF レーザー(300mj/cm²p)照射による内部透過率変化 (T%)
A-6	1	2.1×10^{17}	○	20.5
A-7	10	1.2×10^{18}	○	9.8
A-8	50	2.1×10^{19}	○	5.1
A-2	100	5.5×10^{19}	○	3.8
A-9	200	8.9×10^{19}	○	2.9

[Drawing 5]



[Drawing 6]



[Drawing 8]

Sample No.	熱処理時間 (時間)	外周から20mm部分の水素濃度 (molecules/cm³)	中央部分の水素濃度 (molecules/cm³)	Δn
C-1	50	1.5×10^{19}	5.8×10^{18}	9×10^{-4}
C-2	100	1.2×10^{19}	5.2×10^{18}	4×10^{-4}
C-3	200	9.0×10^{18}	4.8×10^{18}	3×10^{-4}
C-4	300	7.0×10^{18}	3.9×10^{18}	2×10^{-4}
C-5	400	5.1×10^{18}	3.2×10^{18}	2×10^{-4}

[Drawing 12]

第3工程終了後
$\Delta n = 3\times10^{-4}$

[Drawing 9]

Sample No.	熱処理時間 (時間)	外周から20mm部分の水素濃度 (molecules/cm³)	中央部分の水素濃度 (molecules/cm³)	Δn
C-6	30	1.4×10^{19}	5.8×10^{18}	9×10^{-4}
C-7	60	1.2×10^{19}	5.1×10^{18}	4×10^{-4}
C-8	120	8.8×10^{18}	4.9×10^{18}	3×10^{-4}
C-9	180	6.9×10^{18}	3.7×10^{18}	2×10^{-4}
C-10	240	4.9×10^{18}	3.0×10^{18}	2×10^{-4}

[Translation done.]